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(54) Title: REGIO-REGULAR FUNCTIONALIZED POLYMERIC PACKAGING MATERIAL

(57) Abstract

    The present invention is directed to Packaging Materials and Packaging Articles having a structure composed of a substantially linear, regio-regular functionalized hydrocarbon polymer having C_4-C_{12} hydrocarbon polymer repeating units wherein each unit has at least one functional group uniformly pendent therefrom.

OXYGEN BARRIER PROPERTY COMPARISON

PERCENT RELATIVE HUMIDITY

OXYGEN PERMEABILITY (cc.mil/m2.day.atm)

—✕— POLYMER H   —□— POLYMER G   —✳— POLYMER B
—△— POLYMER E   —◇— POLYMER D   —○— POLYMER C
—■— POLYMER 2   —●— POLYMER 3

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REGIO-REGULAR FUNCTIONALIZED
POLYMERIC PACKAGING MATERIAL

BACKGROUND OF THE INVENTION

10   The present invention is directed to films, coatings and articles useful in

packaging applications, especially in the packaging of oxygen-sensitive materials, such

as foodstuff and medicaments.

Packaging articles, whether in the form of a film (single or multi-layer), or

structural design which may be flexible, semi-rigid, rigid and which may be of a lidded

15   or collapsible design ("Packaging Article"), serve not merely to contain the substance

being packaged but, depending on the nature of the substance, to also prevent ingress of

harmful matter from the environment or, alternately, of egress of volatiles within a

Packaging Article.

Oxygen from the atmosphere has long been recognized as one of the most

20   harmful matter for many packaged materials, especially foodstuffs. Thus, the teaching

herein shall be mainly directed but not limited to Packaging Articles which have high

oxygen barrier properties due to having, as part of the Article's structure, a hydroxy-

functionalized, regio-regular hydrocarbon polymer. Packaging Articles which comprise

subject regio-regular polymer having certain other functional groups, as described

25   herein, provide Articles with other desired properties, as fully disclosed herein below.

In packaging oxygen sensitive substances, such as foodstuffs, beverages, and

pharmaceuticals (collectively "products"), oxygen contamination can be particularly

troublesome. Care is generally taken to minimize the introduction or concentration of

oxygen or to reduce the detrimental or undesirable effects of oxygen on the foodstuff or

30   beverage.

Molecular oxygen (O_2) can be reduced to a variety of intermediate species by

the addition of one to four electrons; these species are superoxide, hydroxy radical,

hydrogen peroxide, and water. O_2 and water are relatively unreactive. However, the

three intermediate species are very reactive. Also, O_2 can be activated to single electron state oxygen (which can undergo subsequent reduction to the more reactive oxygen species) by irradiation, or by the presence of catalytic agents. These reactive oxygen species are free radical in nature, and the oxidative reactions in which they

5   participate are therefore autocatalytic.

Carbon-carbon double bonds are particularly susceptible to reaction with the intermediate species. Such carbon-carbon bonds are often found in foods and beverages, pharmaceuticals, dyes, photochemicals, adhesives, rubbers and polymer precursors. Virtually any product which has complex organic constituents will contain

10   such carbon-carbon double bonds or other oxygen reactive components, and hence are susceptible to undergoing oxidative reactions. Thus, if the oxidation products adversely affect the quality performance, odor or flavor of the packaged product, then preventing oxygen ingress into a Packaging Article will greatly benefit the packaged products storage life and usefulness.

15   A number of strategies exist to deal with oxygen which is contained within a Packaging Article's free void space. The most basic is to remove the oxygen by vacuum or by inert gas sparging or both. More recently, oxygen scavenger compositions have been added to polymeric gasket compositions used in certain elements of Packaging Articles (e.g., bottle caps and can closures) as well as in one or

20   more layers of polymeric films used to form Packaging Articles. Such scavenger compositions address the need to remove oxygen from the interior of a closed Packaging Article by reacting or combining with the entrapped oxygen or with oxygen which may enter the Packaging Article during transportation or storage. Although the methods and compositions described above address the concerns with entrapped

25   oxygen, they do not primarily address the problems associated with entry of oxygen and other contaminants into a Packaging Article from the exterior environment.

Glass and metals provide packaging materials which have extremely good barrier properties with respect to the ingress of substances from the exterior environment. However, these packaging materials are costly, provide Packaging

30   Articles which are heavy, rigid in construction and, in the case of glass, are breakable.

Polymers have also been used extensively in packaging applications where they have many advantages over the use of glass or metal. The advantages are derived from

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the diversity of polymers themselves in their mechanical, thermal, chemical resistance and optical properties and from the diversity and adaptability of fabrication techniques which can be employed. Thus, flexible bags, semi-rigid and rigid containers as well as clinging and shrinkable films can be made into Packaging Articles which have walls of
5   homogeneous, laminated or coated structure.

Further, packaging materials and the articles may be formed of a single layer (one composition throughout its thickness) or as a multi-layer structure wherein different layers of the structure are present to provide a combination of desired properties. For example, one or both surface layers may be composed of polymer(s)
10   having groups which provide sealing properties. Other layers may be formed of polymers having high tensile strength to impart tear resistance to the resultant film and article. Similarly, polymers or blends of polymers may be used in different layers of a multi-ply material to impart gas barrier properties, printability characteristics, strength, heat shrink properties, adhesion between other layers which otherwise have poor
15   adhesion properties to each other, as well as other properties desired of the resultant Packaging Article.

It has been presently found that improved packaging materials can be formed by utilizing certain polymers which have functional groups capable of contributing a particular property and where the structure of the polymers have a substantially linear
20   hydrocarbon backbone chain (is substantially devoid of side chains) and has a substantially uniform sequence of atoms along the polymer chains. It has been further found that improved packaging materials can be formed from certain linear polymers which have a uniform sequence of atoms along the polymer chain and have functional groups substantially uniformly pendent therefrom (regio-regular structure). It has been
25   still further found that improved packaging materials can be formed from said regio-regular hydrocarbon polymers which have functional groups pendent from vicinal carbons along the chain (i.e., the functional groups are present in a head-to-head configuration).

Thus, it is the object of the present invention to provide packaging materials and
30   Packaging Articles formed therefrom comprising a regio-regular, linear hydrocarbon polymer having a structure comprising pendent functional groups uniformly distributed along the polymer chain.

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It is also an object of the present invention to provide packaging materials and Packaging Articles formed therefrom comprising a regio-regular, linear hydrocarbon polymer having a structure comprising vicinal pendent functional groups uniformly distributed along the polymer chain.

5   It is a further object of the present invention to provide packaging materials and Packaging Articles formed therefrom having a structure composed of at least one layer wherein at least one of said layer(s) of the structure comprises a functionalized, linear, regio-regular hydrocarbon polymer.

It is still further an object of the present invention to provide packaging material

10   and Packaging Articles formed therefrom having a structure composed of at least one layer wherein at least one of said layer(s) of the structure comprises a hydroxyl functionalized, linear, regio-regular hydrocarbon polymer and, preferably wherein the hydroxyl groups are pendent from vicinal carbon atoms of the polymer chain.

It is further an object of the present invention to provide packaging material and

15   Packaging Articles formed therefrom which are capable of exhibiting very low degrees of gas (e.g., oxygen) permeability and are capable of having said low permeability irrespective of environmental moisture content.

FIGURES

20   Figure 1 is a graphical representation of oxygen permeability versus environmental moisture (relative humidity) for monolayer packaging films formed from commercially known oxygen barrier polymers and for a vicinal dihydroxy linear regio-regular hydrocarbon polymer, as taught herein. Polymers C-H are commercial polymers used here for comparative purposes. Polymer "C" is a polyacrylonitrile

25   copolymer (Barex 210 of British Petroleum); Polymer "D" is a nylon polymer of meta-xylenediamine-co-adipic acid (MXD6 of Dupont); Polymer "E" is a polyvinylidene chloride (Saran® of Dow); Polymers "B", "F" and "G" are ethylene-vinyl alcohol copolymers having 56, 68 and 73 mole percent vinyl alcohol, respectively, (EVALCO Products E151A, F Series, and L Series). Polymers "B", "F" and "G" are each non-

30   linear copolymers which do not have a regio-regular structure. Polymer "7" is a vicinal dihydroxy functional, linear regio-regular polymer formed by ring-opening metathesis polymerization (ROMP) of 1,2-dihydroxycyclooct-5-ene followed by hydrogenation.

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Figure 2 is a carbon-13 nuclear magnetic resonance spectrum of a substantially linear, regio-regular, vicinal hydroxyl group functionalized polymer formed by ROMP of 1,2-dihydroxycyclooct-5-ene followed by hydrogenation, which polymer has been found useful in forming packaging materials and articles of the present invention.

5   Figure 3 is a carbon-13 nuclear magnetic resonance spectrum of commercially obtained ethylene-vinyl alcohol copolymer having 56 mole percent vinyl alcohol units (Polymer "B" above). This spectrum is for comparative purposes with respect to the spectrum of Figure 2 of a polymer having comparable hydroxyl content.

10   SUMMARY OF THE INVENTION

The present invention is directed to packaging materials and Packaging Articles which have, as part of their structure, a functionalized, linear, regio-regular hydrocarbon polymer. The packaging material may be comprised of one layer or a plurality of layers provided at least one layer of the material and of the resultant article comprises the

15   functionalized, linear, regio-regular hydrocarbon polymer, preferably wherein the polymer functional groups are pendent from vicinal carbon atoms of the hydrocarbon polymer backbone chain.

DETAILED DESCRIPTION

20   The packaging material and Packaging Articles of the present invention shall be described in terms of such material and articles which have a thickness which comprises a substantially uniform composition from one surface to the other surface forming the bounds of the thickness (i.e., a single ply or monolayer structure) as well as material and articles which have a thickness comprising a plurality of layers (i.e., a

25   multi-ply or multi-layer structure). Further, the present invention shall address the layer or layers of the structure which utilize the presently described functionalized polymers which are substantially linear, have regio-regular structure with respect to the polymer's hydrocarbon backbone chain and, preferably, have functional groups in a regular head-to-head relationship to each other (the functional groups are pendent from adjacent

30   carbon atoms of the polymer's hydrocarbon backbone chain). The remaining layer(s) forming a multi-layer material can be chosen from any known composition used in packaging applications known to one reasonably skilled in the art to provide a multi-

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layer packaging material and article. The subject material and structure formed
therefrom may be used to form part or substantially all of the subject Packaging Article.

The present invention is directed to packaging materials and articles which
utilize a substantially linear, regio-regular functionalized hydrocarbon polymer. Such
5   polymers have regular repeating units which can be represented by the formula:

$$\underset{[CH_2(CR_2)_a\ \overset{\displaystyle X}{\overset{\displaystyle |}{CH}}\ \overset{\displaystyle Y}{\overset{\displaystyle |}{CH}}]_n}{\qquad\qquad\qquad\qquad\qquad I}$$

10
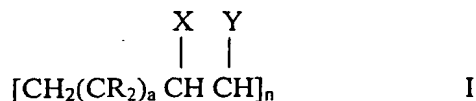
wherein

X and Y each independently represents hydrogen, a C_1-C_5 alkyl, or a functional
group selected from a hydroxyl group, carboxylic acid group, carboxylic acid ester
group of a C_1-C_5 alkyl, acetate group, amide group, nitrile group or carbonyl group;
15   provided at least one of the X and Y groups of each unit of the polymer represents one
of said functional groups and, preferably both X and Y groups of each unit of the
polymer represent functional groups;

each R independently represents hydrogen atom or a C_1-C_5 alkyl, preferably
hydrogen;
20   "a" represents an integer of 1 to 9, preferably 1, 2 or 4-9 and more preferably 1,
2, 5, 7, or 9; and

"n" represents an integer from 5 to 5000 and preferably from 10 to 3000.

Thus, the subject polymer is substantially linear, has a hydrocarbon polymer
backbone chain, has repeating units along said chain and comprises at least one
25   functional group (preferably two groups on vicinal carbon atoms) regio-regularly
positioned along the polymer chain.

Functionalized regio-regular hydrocarbon polymers having small repeating units
can be formed by acyclic diene metathesis polymerization, as described by Valenti and
Wagener, in Macromolecules (1998) 31, 2764-2773; by ring opening metathesis
30   polymerization, as described by Hillmeyer, Laredo and Grubbs, in Macromolecules
(1995) 28, 6311-6316; by hydroboration of unsaturated polymers to provide mono
hydroxy functional polymers, as described by Ramakrishnan in Macromolecules (1991)
24, 3753-3759 and by Ramakrishnan and Chung in Macromolecules (1990) 23, 4519-

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4524; and by ring opening metathesis polymerization of 3,4-capped difunctional
cyclobutene to provide an unsaturated polymer, as described by Perrott and Novak in
Macromolecules (1995) 28, 3492-3494 which, after removal of the protective cap
group, can be converted to the saturated polymer by hydrogenation. The teachings of

5   each of the above cited articles are directed to synthesis processes for forming such
polymers and, such teachings are incorporated herein in their entirety by reference.

In addition to the above-described synthesis, certain functionalized regio-regular
polymers prepared by ROMP of functionalized C_7-C_{12} cyclic olefins have been
described in copending U.S. patent application having Serial Number 09/052,079, filed

10   March 31, 1998, the teachings of which are incorporated herein in its entirety by
reference. The polymers of this co-pending application, in particular those having
vicinal functional groups are preferred polymers to be used in forming the present
Packaging Articles.

The packaging materials and the Packaging Articles of the present invention

15   comprise a structure of at least one layer (one or more than one layer) wherein at least
one of said layer(s) is formed of a composition comprising a functionalized, regio-
regular hydrocarbon polymer or a mixture thereof. The regio-regular polymers used
herein preferably have substantially all vicinal configuration of functional groups
pendent from the polymer backbone chain. The subject polymers can be formed by

20   ring-opening metathesis polymerization (ROMP) of a C_5 or C_7-C_{12} cyclic olefin having
at least one and, more preferably, vicinal functional groups pendent from the ring
carbon atoms. The formed polymer may then be hydrogenated to provide a
substantially straight chain alkylene resultant polymer having pendent functional groups
(preferably configured head-to-head) periodically distributed along the polymer chain.

25   Alternately, the polymer formed by ROMP may be partially hydrogenated to provide a
resultant polymer which also has ethylenic unsaturation periodically as part of the
hydrocarbon backbone structure. These polymers exhibit enhanced properties which
make them useful in forming packaging materials and articles.

The polymer used in the subject packaging material and article can be formed

30   from a functionalized C_5 or C_7-C_{12} cyclohydrocarbon having one olefinic unsaturation
group as part of the ring structure. The functionalized cyclohydrocarbon may, for
example, be selected from cyclopentene, cycloheptene, cyclooctene, cyclononene,

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cyclodecene, cyclohendecene, cyclododecene and the like. The preferred functionalized cyclohydrocarbons are those having five, eight, ten or twelve carbon atoms making up the ring. The resultant polymer I thus has repeating units wherein "a" is equal to 2, 5, 7, or 9, respectively. The term C_5 and C_7-C_{12} refers to the number of

5   carbon atoms forming the ring structure of the functionalized cyclic olefin.

The functionalized polymer used herein can be formed from an unsaturated cyclohydrocarbon having at least one functional group pendent from a carbon atom of the ring starting material. Preferably, the cycloalkene starting material and the resultant polymer should have vicinal functional groups pendent from carbon atoms of the ring

10   and of the polymer's backbone chain, respectively. The teachings made in referenced copending application, U.S. Serial No. 09/052,079, with respect to the functionalized cycloolefin starting material, the resultant polymer, and the method of forming same are also applicable with respect to starting material and polymer having only one functional group per repeating unit (region) of the regio-regular polymer. Where the functional

15   group can be either one or more than one group in a region, the teachings of the referenced copending application can be viewed as having X of Formula II, IV and V herein below as representing hydrogen or a functional group, and is preferably a functional group, as stated in the copending referenced U.S. patent application. In either case, at least one carbon which is adjacent to the olefinic group of the ring must

20   be free of functional groups. That is, when numbering the ethylenic carbons 1 and 2, the next carbon and, preferably, the carbon having the highest number defining the ring should not contain pendent groups except for hydrogen atoms. The cyclohydrocarbon, in addition to the functional groups stated above, may contain hydrocarbon or functional groups pendent from other carbon atoms of the ring except for at least one

25   carbon atom of the ring which is adjacent to the ethylenic group, as described above.

In general, cyclic olefins useful in providing the regio-regular polymer used herein is a functionalized, cycloalkene which can be represented as:

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$$
\text{II}
$$
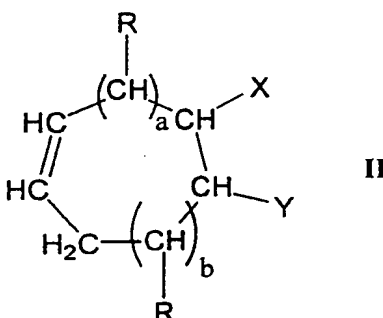
wherein at least one carbon atom which is alpha with respect to the ethylenic group has

5   only hydrogen atoms pendent therefrom. X represents hydrogen or a C_1-C_5 alkyl or Y;

and Y represents a functional group selected from hydroxyl, carboxylic acid, carboxylic

acid esters of a C_1-C_5 alkyl, acetate, amide, nitrile or carbonyl group. It is preferred that

X and Y represent functional groups and that they are the same functional group. The

symbol "a" is a value of 0 to 6 and "b" has a value of 0 to 6 provided the sum of a+b is

10   a value of 0 or an integer between 2 and 7. Each R pendent from the ring carbon atoms

of "a" and "b" can independently represent a hydrogen atom, a C_1-C_5 (preferably a C_1-

C_2) alkyl group or a functional group, as described above.

The packaging material and Packaging Article of the subject invention shall be

discussed herein below primarily in terms of utilization of hydroxylated polymers

15   (where X or Y; or both X and Y represent an -OH group). These polymers can be

viewed as copolymers of vinyl alcohol and an alkylene. such as ethylene, linear

propylene and the like. For example, it has been found that ROMP of 1,2-

dihydroxycyclooct-5-ene provides a polymer which, after hydrogenation, can be viewed

as a copolymer of ethylene and vinyl alcohol wherein the vinyl alcohol units are

20   arranged strictly in a head-to-head configuration. Ethylene/vinyl alcohol (EVOH)

copolymers are commonly available and have been used in packaging materials and

articles. However, these known polymers are formed by free radical copolymerization

of ethylene and vinyl acetate followed by hydrolysis of the acetate groups to hydroxyl

groups. The conventional EVOH copolymer contains each vinyl alcohol monomeric

25   unit randomly distributed along the polymer chain, the hydroxyl groups (disregarding

residual acetate groups) are generally configured head-to-tail when part of adjacent

monomeric units and the polymer contains considerable short and long chain branch

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chains. In contrast, the preferred hydroxy-containing polymer provided by the present

invention (a=2; b=1; X and Y=OH, each R=H) can be viewed as analogous to an

ethylene/vinyl alcohol copolymer with the unique feature of having ethylene and vinyl

alcohol pairs of monomeric units in a sequential arrangement of ethylene-vinyl

5   alcohol/vinyl alcohol-ethylene along the polymer chain. Further, the adjacent vinyl

alcohol units are only in a head-to-head configuration. Figure 2 is an NMR spectrum of

the regio-regular polymer used herein while Figure 3 is an NMR spectrum of

commercial EVOH copolymer having substantially the same OH content.

        Another example is the formation of a polymer by the ROMP of 4-cycloocten-1-

10   ol to provide a polymer which, after hydrogenation, can be viewed as a copolymer of

ethylene and vinyl alcohol having 25 mole percent vinyl alcohol units. Again, EVOH

copolymers having 25 mole percent vinyl alcohol are commercially available but differ

from that presently used. The commercial materials have the vinyl alcohol units

randomly distributed along the polymer chain and have a branched structure instead of a

15   substantially linear, regio-regular configuration.

        Alternately, hydroxy functionalized substantially regio-regular, linear polymer

can be formed through the hydroboration/oxidation of cis-1,4-polybutadiene according

to the procedure of Ramakrishnan, supra. It is well known that polymerization of 1,3-

butadiene to cis-1,4-polybutadiene provides a linear hydrocarbon polymer having one

20   olefinic unsaturation for each four carbon atom repeating unit of the polymer backbone

chain. The olefinic units, uniformly distributed along the polymer chain, can be reacted

by hydroboration/oxidation in the manner described by the Ramakrishnan references

cited above to provide a single hydroxyl functional group for every four carbon atoms.

Thus, the resultant polymer can be again viewed as an ethylene/vinyl alcohol copolymer

25   wherein the vinyl alcohol units are substantially uniformly (regularly) distributed along

the polymer chain and the polymer hydrocarbon backbone is substantially linear and

composed of repeating regions of four carbon units. Again, such polymers are distinct

from the commercial counterpart formed from ethylene and vinyl acetate, as discussed

above. Similar to its higher regio-unit hydroxyl functional polymer described in

30   copending U.S. application Serial no. '079, the use of this linear, regio-regular polymer,

poly(hydroxybutylene), has been found to provide a high degree of gas barrier

properties and other desired physical properties not achievable by conventional

materials of similar hydroxyl content.

Other functionalized polymers which can be used herein can be prepared in the

manner fully described in the referenced copending application, U.S. application Serial

5   No. 09/052,079, and herein below. The starting monomer compound. a functionalized

C_5 or C_7-C_{12} cycloalkene (wherein C_5 and C_7-C_{12} refers to the number of ring carbon

atoms) represented by the formula

II
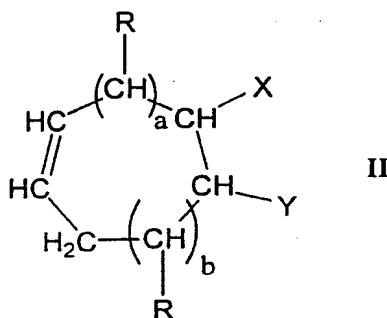
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wherein X represents hydrogen, a C_1-C_5 alkyl or Y; and Y represent functional groups,

as described above and preferably X and Y both represent the same functional group,

15   "a" represents a numerical value of 0 to 6 and "b" represents a numerical value of 0 to

6, provided the sum of a+b is a value of 0 or an integer of from 2 to 7. Each R of the

ring carbon atoms of "a" and/or of "b" may be unsubstituted (preferred) or further

substituted, as described above. When X and Y are both functional groups, X and Y

groups may be sterically positioned on the same side or opposite sides of the plane

20   bisecting the ring carbon atoms except in the case of X and/or Y being a carbonyl

group. in which case the group would be substantially within the plane of the ring. In

other words, X and Y may be either in a cis or trans configuration with respect to each

other.

The formation of the preferred difunctional cycloalkenes (II) found useful herein

25   can be achieved by known methods. For example, 5-cyclooctene-trans-1.2-diol can be

prepared by reacting the monoepoxide of 1,5-cyclooctadiene with perchloric acid in an

aqueous solution at elevated temperatures as taught in French Patent 1,294.313 which

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teaching is incorporated herein in its entirety by reference. Other methods of

preparing the vicinal dihydroxy functionalized cycloalkene include reacting the

cycloalkadiene monoepoxide with acetic acid and potassium acetate to initially form the

hydroxy/acetate compound followed by saponification; oxidation of cycloalkadiene

5   with peroxide and formic acid followed by basic hydrolysis [Yates et al., Canadian

Journal of Chemistry, Vol. 50, 1548 (1972)]; reacting a cycloalkadiene monoepoxide

with an organic acid, such as formic or acetic acid to form the hydroxy/acetate

compound followed by saponification [McIntosh, Canadian Journal of Chemistry, Vol.

50, 2152 (1972)]; or reacting a cycloalkadiene with osmium tetroxide in ether/pyridine

10   solution at low temperatures followed by reflux with sodium sulfite in water/alcohol

[Leitich, Tetrahedron Letters, No. 38, 3589 (1978)].

        A vicinal dione cycloalkene can be formed from the vicinal diol according to the

procedure described by Yates et al., Canadian J. of Chem., Vol. 50, 1548 (1972).

        The vicinal hydroxy/ketone cycloalkene and the vicinal ketone/acetate

15   cycloalkene are formed by oxidizing the hydroxy/acetate with chromic acid in acetone

at low temperatures (e.g., 0-10°C) to form the ketone/acetate. The ketone/acetate

cycloalkene can be recovered by distillation. The ketone/acetate can be converted to

the vicinal hydroxy/ketone cycloalkene by hydrolysis with sodium hydroxide in

methanol at slightly elevated temperatures (e.g., 40°C).

20   The monoepoxy cycloalkene, which is the precursor of several of the synthetic

routes described above can be obtained by catalytic oxidation of a cycloalkadiene using

a peroxide and sodium tungstate as the catalyst as described by Venturello, in J. Org.

Chem., 48, 3831 (1983) and J. Org. Chem., 53, 1553 (1988). Other methods of forming

the mono-epoxy cycloalkene are disclosed by Grubbs, Macromolecules, 28, 6311

25   (1995); Camps, J. Org. Chem. 47, 5402 (1982); Imuta, J. Org. Chem. 44, 1351 (1979);

Murray, Org. Syn., 74, 91 (1996); and Payne, Tetrahedron, 18, 763 (1962).

        The teachings of each of the above cited references is incorporated herein in its

entirety by reference.

        The functionalized cycloalkene can be subjected to ring opening metathesis

30   polymerization using a well-defined ROMP catalyst. Such catalysts found useful herein

are disclosed by Schrock et al in JACS 1990, 112, 3875; and U.S. Patents 4,681,956;

5,312,940; and 5,342,909. The preferred catalysts are those described in U.S. Patent

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5,312,940. The teachings of each of the above references is incorporated herein in its entirety by reference.

One class of ROMP catalyst found useful in providing the present polymers can be represented by the general formula:

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$$M(NR^1)(OR^2)_2(CHR^3) \qquad\qquad III(a)$$

wherein:

M is molybdenum or tungsten;

10 R^1 and R^2 of Formula III(a) are independently selected from alkyl, aryl, aralkyl or halogen-substituted derivatives or silicon-containing analogs thereof. Examples of aryl groups are phenyl, 2,6-diisopropylphenyl and 2,4,6-trimethylphenyl. Examples of aralkyl groups are benzyl and triphenylmethyl. Examples of R^1 in Formula IIIa are 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl, 2,6-di-t-butylphenyl, pentafluorophenyl, t-

15 butyl, trimethylsilyl, triphenylmethyl, triphenylsilyl, tri-t-butylsilyl, and perfluoro-2-methyl-2-pentyl and the like. Examples of R^2 in Formula IIIa are t-butyl, trifluoro-t-butyl [(CF_3)(CH_3)_2C], perfluoro-t-butyl, perfluoro-2-methyl-2-pentyl, 2,6-diisopropylphenyl, pentafluorophenyl, trimethylsilyl, triphenylsilyl, tri-t-butylsilyl, and hexafluoro-t-butyl [(CF_3)_2(CH_3)C] and the like. R^3 of Formula III(a) is selected from

20 an alkyl, aryl, aralkyl or any substituent that results from the initial reaction between the $M=CHR^3$ complex and the olefin(s) that is(are) being metathesized, alkyl has 1-20 carbons, aryl has 6-20 carbons and aralkyl has 7-20 carbons; R^3 is preferably t-butyl or phenyl, but since the M-CHR^3 moiety of the compound of Formula IIIa is intimately involved in the catalytic reaction, it is recognized that the CHR^3 ligand is replaced by

25 any other alkylidene fragment from the olefins that are being metathesized.

The catalyst IIIa should not be used with monomer II which has a proton on the functional group, that is, for example hydroxyl, carboxylic acid and the like. It may be used where ester, acetate, carbonyl and the like groups are present.

The preferred ROMP catalysts are those represented by the general formula:

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$$X \underset{X^1}{\overset{L}{\underset{L^1}{\big|}}} M = C \underset{R^1}{\overset{R}{\big\langle}} \qquad \text{IIIb}$$
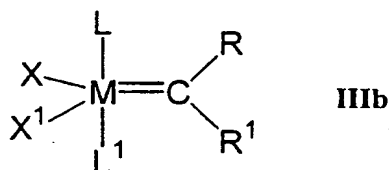
wherein:

M is selected from Mo, W, Os or Ru; and preferably Ru or Os; and most preferably Ru;

R and R^1 are independently selected from hydrogen; C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_1-C_{20} alkyl, aryl, C_1-C_{20} carboxylate, C_1-C_{20} alkoxy, C_2-C_{20} alkenyloxy, C_2-C_{20} alkynyloxy, aryloxy, C_2-C_{20} alkoxycarbonyl, C_1-C_{20} alkylthio, C_1-C_{20} alkylsulfonyl or C_1-C_{20} alkylsulfinyl; each optionally substituted with C_1-C_5 alkyl, halogen, C_1-C_5 alkoxy or with phenyl group optionally substituted with halogen, C_1-C_5 alkyl or C_1-C_5 alkoxy; preferably R and R^1 are independently selected from hydrogen; vinyl, C_1-C_{10} alkyl, aryl, C_1-C_{10} carboxylate, C_2-C_{10} alkoxycarbonyl, C_1-C_{10} alkoxy or aryloxy; each optionally substituted with C_1-C_5 alkyl, halogen, C_1-C_5 alkoxy or with a phenyl optionally substituted with halogen, C_1-C_5 alkyl or C_1-C_5 alkoxyl;

X and X^1 are independently selected from any anionic ligand; preferably X and X^1 are independently selected from halogen, hydrogen; C_1-C_{20} alkyl, aryl, C_1-C_{20} alkoxide, aryloxide, C_3-C_{20} alkyldiketonate, aryldiketonate, C_1-C_{20} carboxylate, aryl or C_1-C_{20} alkylsulfonyl or C_1-C_{20} alkylsulfinyl; each optionally substituted with C_1-C_5 alkyl, halogen, C_1-C_5 alkoxy or with a phenyl group optionally substituted with halogen, C_1-C_5 alkyl or C_1-C_5 alkoxyl;

L and L^1 are independently selected from any neutral electron donor, preferably L and L^1 are independently selected from phosphine, sulfonated phosphine, phosphite, phosphinite, phosphonite, arsine, stilbene, ether, amine, amide, sulfoxide, carbonyl, nitrosyl, pyridine or thioether; and

wherein any 2, or 3 of X, X^1, L, L^1 may be optionally bonded together to form a chelating multidentate ligand.

The ROMP of a functional C_5 or C_7-C_{12} cycloalkene (II) may be carried out neat or by providing a solution of (II) in a hydrocarbon solvent such as, an aromatic hydrocarbon as, for example: benzene or toluene; tetrahydrofuran; dialkyl ethers; cyclic

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ethers; sec-butyl alcohol, tert-butyl alcohol; and the like and halogenated solvents,

such as, halogenated aromatics as well as halogenated alkanes and the like. The

preferred solvents are chlorinated alkanes, such as dichloromethane and the like,

chlorinated aromatics, such as monochlorobenzene and the like. The molar ratio of (II)

5   to catalyst III(b) should be from about 200 to 5,000, preferably from about 400 to 3000.

The ROMP reaction may be carried out at temperatures of from about 10°C to 75°C

and preferably from about 20°C to 50°C. The most preferred temperature will depend

on the particular starting material, the ROMP catalyst, and the solvent used and can be

determined by minor experimentation and is usually in the range of from 35 to 50°C.

10   The time dedicated to carrying out the ROMP reaction may range from only a few

minutes to about 48 hours. The reaction time is normally from 2 to 30 hours, with 10 to

20 hours being preferred. The molecular weight of the formed polymer product can be

regulated by (a) altering the monomer II to catalyst III(b) ratio, and/or by (b)

introducing a suitable acyclic olefin in small amounts to act as a chain transfer agent.

15   Such agents should be soluble in the polymerization reaction media or monomer used

and may be, for example, cis-3-buten-1-ol, cis-3-hexen-1-ol and the like. When used,

the chain transfer agent (CTA) should be present in molar ratio of monomer II to CTA

of from about 50 to 2000 and preferably from about 200 to 1000.

ROMP of the functional cycloalkene (II) above provides a polymer having

20   repeating units of the general formula:

$$-\left[CH=CH-\left(CHR\right)_a-CHX-CHY-\left(CHR\right)_b-CH_2-\right]_n \quad\quad IV$$
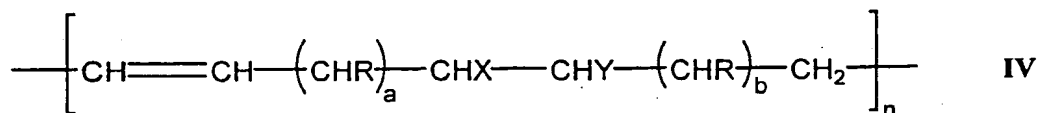
25   wherein X, Y, a and b are the same as defined for Formula I above and each R

independently represents hydrogen or a C_1-C_5 alkyl or a Y group. It should be noted

that the ROMP process of the preferred cycloalkene (II) provides a polymer IV having

vicinal functional groups X and Y, the polymer chain is substantially linear, and the

chain further contains an ethylenic unsaturation spaced (a) carbon atoms from the X

30   functional group. In the polymer, groups X and Y may have the same or opposite

stereo-configuration to that of the cyclic monomer used. Similarly, the polymer product

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IV has double bonds which normally provide a mixture of both cis and trans geometric isomers (i.e., the alkenyl hydrogen atom may be cis or trans with respect to its nearest alkenyl hydrogen atom neighbor). Further, the above structure IV is the repeating unit of the formed polymer and, thus, does not have any substantial degree of randomness of the X and Y groups and of the alkylene units along the polymer chain.

The polymer product IV can be recovered by introducing a non-solvent into the solution to cause the polymer to precipitate out of solution. Such non-solvents include for example, alkanes (e.g., pentane, hexane, heptane, etc); ketones (e.g., acetone, methyl ethyl ketone, etc.) and the like. The particular non-solvent to be used can be readily determined by the artisan. The polymer product IV can be readily recovered by introducing the polymerization reaction mixture into an excess of a non-solvent liquid.

The preferred conditions and catalyst for performing a ROMP of 5-cyclooctene-trans-1,2-diol are:

Catalyst: Compound III(b) wherein $X=X^1=Cl$

$L=L^1=$tricycloalkylphosphine (e.g.,

tricyclohexylphosphine)

R=phenyl or 1,1-diphenylethenyl

$R^1=$hydrogen

Solvent(s): chlorinated alkanes

(e.g., methylene chloride)

Temperature range: 40-50°C

Time range: 6 to 24 hours

The separated polymer IV can be subjected to conventional catalytic hydrogenation or, optionally, chemical hydrogenation (e.g., using chemical hydrogenation agents, such as para-toluene sulfonyl hydrazide and the like) to provide a substantially completely saturated polymer V. The structure of polymer V repeating units can be represented by the formula:

$$\left[CH_2 - CH_2 - \left(CHR \right)_a - CHX - CHY - \left(CHR \right)_b - CH_2 \right]_n \quad V$$

17
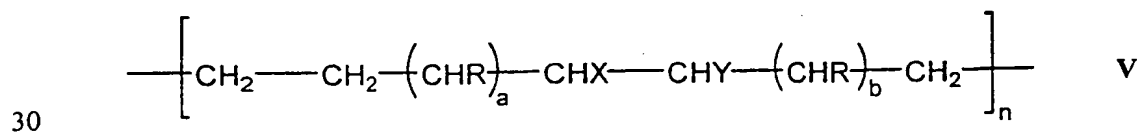
wherein R, X, Y, a and b are as defined for Formula IV above. Alternately, partial hydrogenation can be accomplished by controlling the hydrogenation reaction by known methods. Such methods are known to those skilled in the art and may include controlling the molar ratio of olefinic groups of the polymer to chemical hydrogenation

5   agent, the time of hydrogenation, etc. Where catalytic hydrogenation is employed, the degree of saturation can be controlled by the time and/or hydrogen pressure used. Thus, the resultant polymer V may have residual ethylenic unsaturation to provide sites for grafting, insertion of other functional groups, or for chemical crosslinking for desired reasons. Further, polymers with residual ethylenic unsaturation can be used to form

10   Packaging Articles, such as films, which are subsequently subjected to irradiation, such as electron-beam irradiation to cause cross-linking of the polymer contained within the layer(s) of which it is a part. The amount of residual ethylenic unsaturation will depend on the degree of grafting, insertion or cross-linking desired, the particular treatment being used and the degree of such treatment. In the case of electron beam irradiation it

15   will depend on the radiation dosage and the position of the layer containing the subject polymer within the structure of the Packaging Article. The exact degree of unsaturation which provides the desired property can be determined by simple experimentation by the artisan.

The hydrogenation of the polymer IV can be carried out using conventional

20   hydrogenation, such as Wilkinson's catalyst and the use of hydrogen or the use of other conventional hydrogenation catalysts, such as Raney nickel, palladium on carbon, platinum on carbonate, ruthenium alkylidene complex or the like. The polymer IV is normally dissolved in a solvent or a mixture of solvents such as those described above for the ROMP polymerization and subjected to a hydrogen pressure of at least about

25   300 psi, preferably from about 600 to 5000 psi. The hydrogenation is normally complete in less than 8 hours although shorter or longer times may be utilized. Normally the hydrogenation is carried out for a period of from 2 to 8 hours with from 3 to 7 hours being preferred.

When the ROMP reaction of monomer II is carried out in solution, the resulting

30   solution containing polymer IV can be used directly to carry out the hydrogenation step. Thus, the step of separation of polymer IV from the polymerization medium can be eliminated. Further, it is believed that any ROMP catalyst which may be present in the

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polymer IV solution may aid in the hydrogenation reaction. In a preferred
embodiment, an amount of ROMP catalyst equivalent to that used to achieve the ring-
opening methathesis polymerization reaction is added, after polymerization has been
completed, to catalyze the hydrogenation reaction.

5   An alternate manner of forming regio-regular polymers found useful in forming
packaging materials and Packaging Articles of the present invention is to subject a
monoepoxy C_5 or C_7-C_{12} cycloalkene having at least one (and preferably both) ring
carbon atoms adjacent to the ethylenic unsaturation as an unsubstituted carbon, to
ROMP as described herein above for the vicinal difunctional monomer II. The

10   intermediate polymer product is isolated by precipitation with a non-solvent followed
by further conversion of the epoxy groups to the desired vicinal functional groups
according to the synthetic routes described above. The resultant polymer IV can be
further hydrogenated to provide polymer V in the manner described above.

          Another alternate route in providing regio-regular polymer V for use in the

15   subject packaging material and articles is to first epoxidize the ethylenic unsaturation
units that are substantially uniformly distributed along a linear unsaturated hydrocarbon
polymer chain. Linear unsaturated hydrocarbon polymers having ethylenic units
uniformly distributed within the polymer backbone chain can be formed by ROMP of a
cycloalkene, such as a C_7-C_{12} cycloalkene or a 1,5-cyclooctadiene. The resultant

20   polymer is linear and contains ethylenic unsaturation units which are substantially
uniformly distributed along the chain. These ethylenic units can then be epoxidized by
standard techniques such as catalytic oxidation using a peroxide and a tungstate
catalyst. The epoxy groups can then be converted to the desired vicinal functional
groups, using the synthesis methods described above, to provide polymer product V.

25   Alternately, polymers from ROMP of unfunctionalized cycloalkenes can be subjected to
hydroboration/oxidation to provide polymers useful in films of the subject invention.

          In addition to forming polymers IV and V from a single monomer II, as
described above, one can form copolymers by ROMP of monomer II having X and Y
groups as described above and ROMP of a comonomer IIa. Comonomer II(a) can be

30   selected from a cycloalkene represented by the formula:

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IIa
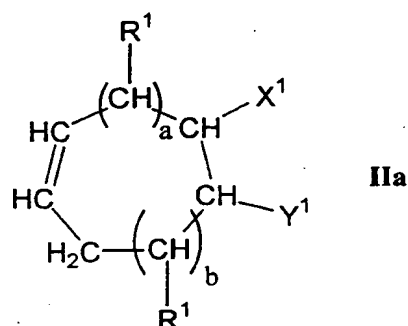
wherein X^1 and Y^1 have the same definition as X and Y described above for monomer

5   II or may be selected (one or both) from hydrogen, provided X^1 and Y^1 together provide

pairs which are distinct from the X and Y pairs of monomer I; R^1 has the same

definition as R of monomer II and a and b are each independently an integer of 0-6

provided the sum of a+b is 0 or 2-7. The copolymerization by ROMP of monomers II

and IIa to provide a linear copolymer of the subject invention can be carried out with

10   molar ratios of II to IIa of from about 50:50 to about 100:0 with from 60:40 to 100:0

being preferred. Because the ROMP of the present monomer is substantially a living

polymerization, one can introduce monomer II and monomer IIa sequentially into the

polymerization reaction media to provide block(s) of units I defined above and block(s)

of units I wherein X and Y are as defined immediately above for IIa. Thus a regio-

15   regular block copolymer product is formed which is linear and preferably has vicinal

functional units uniformly spaced in a head-to-head configuration at least along a

portion of the polymer chain (derived from monomer II) and a second segment of the

polymer chain possibly having a second set of vicinal functional units uniformly

configured along a portion of the same polymer chain (derived from monomer IIa).

20   This block copolymer may be hydrogenated, as described above for the homopolymer.

The above referenced polymers have been compared to their counterpart

copolymer formed by conventional free-radical polymerization and hydrolysis and have

been observed to have superior elongation properties as well as enhanced toughness,

lower melting temperature and lower density. The polymers have been found useful in

25   forming films, coatings, laminates, moldings and the like, for packaging applications.

For example, regio-regular hydroxy functional polymers (both where structure I, X=H;

Y=OH and R=H; and where X and Y each equal OH and R=H) formed according to the

present invention have been found to have superior toughness, flexibility and elongation properties. and very low and uniform gas permeability properties not achievable with analogous conventional free radical formed copolymers having comparable hydroxyl content. Further, when the functional group Y or groups X and Y

5 are carboxylic acid ester groups, the resulting regio-regular linear polymer provides a packaging material having good heat seal properties; when such group(s) are free carboxylic acid groups, the resultant regio-regular linear polymer provides tie (adhesion) properties to bond together distinctly different layers of a multi-ply material; when such group(s) are amide groups, the resultant polymer provides a packaging

10 material which has good protein adhesion and good ink adhesion properties to permit printing thereon; and when such groups are carboxylic acid groups they may be treated with an alkali or alkaline earth or zinc metal base or oxide to provide ionomeric units which provide a packaging material having good anti-fogging, heat-sealability and protein adhesion properties.

15 As indicated above, the regio-regular polymer forms at least one layer of the packaging material and Packaging Articles of the subject invention. When the material and article are of a single layer structure, such materials and/or articles can be formed by extrusion, injection molding or extrusion/thermoforming processes. When the material and article are of a multi-layer structure. they are typically formed using co-

20 extrusion, coating, lamination, blow molding, coextrusion/thermoforming, extrusion/coating, or extrusion/lamination, as taught in U.S. Patents 5,350,622 and 5,529,833.

The layers of the Packaging Article which contains the subject regio-regular polymer can be formed solely of the regio-regular polymer having the desired

25 functionality for a specific known use. It has been unexpectedly found that material containing such layer has enhanced physical properties, such as flexibility, toughness and elongation as well as functionality (i.e., end-uses) when compared to like packaging material containing a layer of conventional polymer of like functional group content. Alternately, the layer of packaging material which contains the subject regio-regular

30 polymer may be in the form of a composition comprising the regio-regular polymer uniformly distributed or dispersed in another polymer(s). It is preferred that the composition retain a high degree of transparency, as such property is highly desired in

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the packaging art and, further, indicates the compatibility of the particular regio-
regular polymer and the carrier polymer used. Normally, the regio-regular polymer
should be the major component of the composition, preferably being greater than 60
weight percent, and more preferably greater than 75 weight percent. The carrier

5   polymer may be chosen from any thermoplastic polymer such as PVC, EVA, PET, PE,
PP or copolymers thereof. For example, the hydroxyl functionalized regio-regular
polymer V described herein and in the referenced copending application may be
blended with a conventional EVOH copolymer for a particular end-use. The exact
nature of the carrier polymer and the amount to be blended with the regio-regular

10   polymer chosen for use can be readily determined by the artisan depending on end use,
the desire to maintain transparency, and the degree of functionality to be exhibited by
the packaging material and articles.

         With respect to the preferred functionalized, regio-regular hydrocarbon polymer
wherein either X or Y is a hydroxyl group or both X and Y are vicinal hydroxyl groups,

15   the resultant packaging material has been found to have extremely low values of gas
(oxygen) permeability and to maintain said low values independent of moisture content
in the surrounding environs (exterior and interior to the resultant Packaging Article).
The comparative results for the subject vicinal dihydroxyl functionalized regio-regular
polymer versus various commercial ethylene-vinyl alcohol copolymers (having varying

20   vinyl alcohol content), as well as other known gas barrier polymers are illustrated in
Figure 1. The present material is shown to be nearly 100 times more effective as a gas
barrier material than its commercial counterpart EVOH having about 56 mole% vinyl
alcohol (Polymer B).

         The layer of the packaging material containing the subject regio-regular polymer

25   may be of any thickness. The exact thickness will depend on its particular function as
part of the packaging material as well as the structure of the packaging material (film or
semi-rigid or rigid article). With respect to films, the thickness can range from 0.025 to
10 mils, preferably from 0.05 to 8 mils and most preferably from 0.1 to 5 mils. Where
the material is used as, or as part of, a semi-rigid or rigid article, the layer containing the

30   functionalized regio-regular polymer defined herein may range from about 0.025 mil to
10 mils, preferably from 0.05 mil to 8 mils. The exact thickness can be determined by
the artisan for the particular application.

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The composition of the layer comprising the regio-regular polymer defined herein can further contain other components, such as pigments, fillers, clays, exfoliated clays (e.g., nanocomposite utility), stabilizers, processing aids, plasticizers, fire retardants, anti-fog agents, dyestuff and the like. The total quantity of said additives is

5   generally less than 10%, usually less than 5% by weight relative to the total composition. The selection of such components depends largely on the material and article to be formed, its method of formation and its contemplated end use. Selection factors for such components are well known in the art.

The subject packaging material and Packaging Article of the present invention

10   can be composed of a single layer or multi-layer structure wherein at least one layer comprises a functionalized, linear regio-regular hydrocarbon polymer. The polymer may further be crosslinked and/or oriented by stretching (uni or biaxially) as may be desired by those skilled in the art.

A multi-layer packaging material and Packaging Articles can be constructed

15   with a plurality of layers, each of which is selected to perform a particular function. Where a layer is formed of a functionalized polymer, such layer may be formed of the functionalized, linear, regio-regular hydrocarbon polymer contemplated herein wherein said polymer has the appropriate functionality. Thus, for example, a multi-layer packaging material and article may contain a gas barrier layer comprising a hydroxy

20   (preferably the vicinal dihydroxy) functionalized, regio-regular polymer and a sealant layer wherein the functionality is selected from carboxylate ester groups or simply linear low density type polyethylene. In many multi-layer structures, at least one surface layer (and optionally, both surface layers) are structural and protective layers, such as formed from olefinic thermoplastic material as, for example, polypropylene,

25   low density polyethylene, linear low density polyethylene (LLDPE) and the like. An inner layer between the surface layers can include a gas barrier layer as, for example, composed of the vicinal dihydroxy regio-regular polymer described hereinabove and tie layers to provide interply adhesion.

Other examples of multi-layer structures useful for packaging materials and

30   Packaging Articles include two-layer structures composed of a barrier layer (mono-hydroxy or vicinal dihydroxy regio-regular hydrocarbon polymer described above) and a heat sealable layer which may comprise a polyolefin as, for example, ethylene/butene

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copolymers, ethylene/hexene copolymers, ethylene/octene copolymers, ethylene/unsaturated ester copolymer (e.g., ethylene/vinyl acetate or ethylene/alkyl acrylate copolymers) and the like. A three layer structure may comprise the above two layers further having a wear or abuse resistant layer as the surface layer adjacent to the

5   barrier layer to provide an abuse-resistant/barrier/sealant multi-layer structure. The abuse-resistant layer may comprise a polyolefin such as polyethylene, polypropylene and the like. Another multi-layer structure may comprise a layer or more than one layer which is used to ensure or enhance interlaminar bond strength between any or all of the other layers of a packaging material or article (a tie layer). The placement of such tie

10   layer(s) will depend on the other layers used and their inherent adhesion to each other. The tie layer may comprise a copolymer of ethylene and (meth)acrylic acid, or an anhydride-grafted polyolefin, or the like or, alternately may be composed of a conventional adhesive or glue such as a polyurethane (most appropriate where laminate construction is contemplated). The tie layer may be formed of a regio-regular

15   hydrocarbon polymer having carboxylic acid groups pendent therefrom.

The multi-layer structure may also contain an oxygen-scavenging layer. Such layers are normally an internal layer located towards the surface layer which is proximate to the cavity of the Packaging Article. Thus, a material or package of the present invention may, for example, have a structure which comprises abuse-

20   resistant/oxygen barrier/adhesive/oxygen scavenger/sealant multi-layer structure. The scavenger layer is normally composed of a carrier polymer which contains an agent capable of interacting with or absorbing and/or reacting with oxygen from the interior cavity of a Packaging Article.

In any of the above multi-layer structures or other structures suitable for

25   providing a packaging material and Packaging Article, the subject functionalized, linear, regio-regular hydrocarbon polymer contemplated herein and in copending application Serial No. 09/052,079 is used to provide at least one layer formed of polymer of the proper functional groups for the intended functions within the article. It has been unexpectedly found that the present regio-regular, functionalized hydrocarbon

30   polymer provides enhanced functionality and a Packaging Article with enhanced functional and tensile properties.

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The following examples are given for illustrative purposes only and are not meant to be a limitation on the claims, appended hereto. All parts and percentages are by weight unless otherwise indicated.

5   Examples

The molecular weights of the polymers reported below were determined by GPC at 50°C using a Waters Alliance System #4 gel permeation chromatograph equipped with a Waters 41-RI detector. Phenogel 5 columns (2 x linear and 1 x 100Å) were used. The eluent was 1-methyl-2-pyrrolidinone/50mM lithium bromide.

10   Polystyrene narrow molecular weight standards were used for calibration.

The melt flow rate of the polymers is reported as MFI (Melt Flow Index) in grams per 10 minutes. The MFI was determined at 190°C using 2.16 Kg weight according to ASTM D1238 using a CSI MFI-2 melt flow indexer.

The oxygen transmission rate (OTR) of pressed film samples was determined

15   using a Mocon Ox-Tran 2/20 ML module following ASTM D3985-81. The polymer powder was blended with the stabilizers and compression molded into thin films (1-6 mils thick) at 190°C for 5 minutes. A compressive force of 15,000 pounds was applied and subsequently the sample was cooled to ambient temperature at about 15° per minute. The pressed films were dried in a vacuum oven at 80°C and conditioned in a

20   dessicator for at least 24 hours prior to testing.

The mechanical properties were measured using an Instron 4204 tester. Modulus, Yield Stress and Yield Strain were determined at an extension rate of 0.5 inch/min and Maximum Stress, Break Stress, Break Strain and Toughness were measured at a crosshead speed of 10 inch/min. Test samples were compression molded

25   at 190°C for 5 minutes followed by cooling at 15°/min using 20 mil shims. Test films were allowed to condition for at least 24 hours in a dessicator at room temperature prior to testing. The dimensions of the dumb-bell test specimens are 1 inch by 4.5 inches.

Example 1

30   Synthesis of Linear 4-Cycloocten-1-ol Homopolymer and Saturated Derivative

(Monomer/Catalyst Molar ratio =400)

The reaction was carried out in a 2 liter resin kettle fitted with an overhead

stirrer. a thermocouple, argon addition port, and two septum ports for the addition of catalyst and solvent. 450 Grams (3.5 moles) of 1-hydroxycyclooct-4-ene was charged to the resin kettle. The monomer was degassed with full vacuum for a minimum of 30 minutes. 7.25 Grams (0.0088 moles) of phenylmethylenebis(tricyclohexylphosphine)

5   ruthenium dichloride catalyst was weighed into a clean, dry half pint bottle in a dry box and the bottle was capped with a septum before removing from the dry box. The polymer molecular weight was controlled by the monomer/ruthenium molar ratio of 750. Methylene chloride (1.5 liter) was deaerated with argon. 100 Grams of methylene chloride was added via syringe to the bottle catalyst with 1200 Grams of methylene

10   chloride was charged via cannula into the reaction resin kettle. The mixture was stirred vigorously. Once the monomer had completely dissolved, the catalyst solution was added via syringe to the reaction resin kettle. The color changed from purple to orange after several minutes. The reaction was carried out at 40°C for 24 hours under vigorous stirring under an argon atmosphere. As time progressed, the solution became viscous.

15   The reaction was complete after 24 hours. The progress of the ROMP reaction was followed by NMR. The degree of conversion from monomer to polymer was determined by proton-NMR, based on integration of the vinyl protons of the monomer at 5.6 ppm and the vinyl protons of the polymer at 5.3 ppm. Ethyl vinyl ether, 70 grams (0.97 moles) was added to the reaction vessel through a fitting on the top of the kettle to

20   terminate the ROMP reaction. After mixing the vinyl ether, the contents of the reaction kettle was poured into a 4-L beaker. 791 Grams of methanol and 0.45 grams of 2,6-di-t-butyl-4-methylphenol (BHT) were added to the beaker and mixed with a stirring bar until a homogeneous solution was obtained.

The ethylenic unsaturated polymer in the solution prepared above was

25   hydrogenated using tris(triphenylphosphine) rhodium chloride as the catalyst at a hydrogen pressure of 640 psi and a temperature of 60°C for 6 hours. The molar ratio of double bonds in the unhydrogenated polymer to the catalyst was 150 to 1. The final hydrogenated polymer (designated as Polymer 1) had the following molecular weights and melt flow rate: M_n=80,300; M_w=145,800; M_z=246,000; PDI=1.8; MFI= 2.3 g/10

30   min (with 1 wt% Irganox 1076, a commercial antioxidant available from Ciba Specialty Chemicals). The present polymer was compared to conventional ethylene/vinyl alcohol random copolymer having 25 mole percent vinyl alcohol (designated as Polymer A).

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Example 2.
Synthesis of Linear 5-Cycloocten-trans-1,2-diol Homopolymer and Its Saturated Derivative

5　　5-Cyclooctene-trans-1,2-diol (MW = 142.19, 40 grams, 0.28 moles) was transferred to a three-neck, 100 ml resin kettle equipped with a mechanical stirrer, argon inlet and a septa. The monomer was degassed under vacuum for 2 hours. The system was maintained under an argon atmosphere. In an argon filled drybox, the ruthenium catalyst, phenyl-methylene bis(tricyclohexylphosphine) dichloride (0.3087

10　　grams, 0.375 mmoles), was weighed into a septa capped glass vial and dissolved in 10 ml of methylene chloride. The deep purple catalyst solution was injected via syringe into the reaction vessel. Methylene chloride (30 ml) was purged with a vigorous stream of argon for 15 minutes and syringed into the resin kettle. The monomer/solvent solution was stirred vigorously. The reaction mixture was heated to 40°C with an oil

15　　bath under a slow argon atmosphere for 24 hours under vigorous stirring. Subsequently, the resin kettle was removed from the oil bath and the reaction mixture was cooled to ambient temperature. Ethyl vinyl ether (0.754 grams, 1 ml, 10.5 mmoles) was added to the reaction mixture along with 40 ml of tetrahydrofuran and 40 ml of methanol and stirred until complete dissolution. The homogeneous solution was subsequently poured

20　　into a solution of 700 ml of cold acetone and 0.4 g of 2,6-di-tert-butyl-4-methylphenol (BHT) to precipitate the polymer. The polymer was redissolved in 20 ml of tetrahydrofuran and 20 ml of methanol and 0.4 grams of BHT and reprecipitated in cold acetone as previously done. This process was repeated one more time. The polymer was dried overnight in a vacuum oven at 60°C to yield 13.4 grams of a hard solid, yellow

25　　polymer .

12 Grams of the dried ethylenically unsaturated polymer was dissolved in 60 ml of tetrahydrofuran and 60 ml of methanol and 0.5205 grams (0.5625 mmoles) of tris(triphenylphosphine) rhodium chloride [RhCl(PPh₃)] catalyst was added. The mixture was hydrogenated in a 600 ml Parr reactor at 600 psi / 54°C for 6 hours. The

30　　reactor was cooled to ambient temperature and the pressure was vented. The solution was filtered through a fritted funnel and the powdery polymer was rinsed with acetone. The polymer was redispersed in acetone overnight and filtered and washed with acetone

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one more time. The slightly yellow polymeric powder was then dried in a vacuum
oven for 7 hours to yield 11.2 grams of hydrogenated polymer (designated "Polymer
2"). The resulting polymer had the following molecular weights and melt flow rate:
Mn=23,900, Mw=47,000, Mz=78,900, PDI= 2, MFI= >10 g/10 min with 0.1 wt%

5   Irganox 1076 as stabilizer. This polymer was compared to conventional ethylene/vinyl
alcohol random copolymer having about 56 mole percent vinyl alcohol (designated
"Polymer B").

Example 3.

10   ## Synthesis of Linear 5-Cycloocten-trans-1,2-diol Homopolymer and Its Saturated
Derivative

5-Cyclooctene-trans-1,2-diol (MW = 142.19, 30 grams, 0.21 moles) was
transferred to a three-neck, 100 ml resin kettle equipped with a mechanical stirrer,
argon inlet and a septa. The monomer was degassed under vacuum for 45 minutes and

15   kept under an argon atmosphere. In an argon filled drybox, the ruthenium catalyst,
phenylmethylene bis(tricyclohexylphosphine) dichloride (MW= 822.96, 0.2319 grams,
0.2818 mmoles) was weighed into a septa-capped glass vial and dissolved in 30 ml of
argon purged methylene chloride. The molar ratio of monomer to ruthenium was 750.
The deep purple catalyst solution was injected via syringe into the reaction vessel. The

20   reaction mixture was maintained at 40°C under an argon atmosphere for 24 hours under
vigorous stirring. Subsequently, the resin kettle was removed from the heat source and
the reaction mixture was cooled to ambient temperature. Ethyl vinyl ether (0.528 grams,
0.7 ml, 7.3 mmoles) was added to the reaction mixture along with 40 ml of
tetrahydrofuran, 40 ml of methanol and 0.15 grams of 2,6-di-tert-butyl-4-methylphenol

25   (BHT). The mixture was stirred until a homogeneous solution was obtained. The
polymer was subsequently precipitated into a solution of 700 ml of methyl ethyl ketone
(MEK) and 0.15 g of BHT. The polymer was redissolved in 30 ml of tetrahydrofuran
and 30 ml of methanol and 0.15 grams of BHT and reprecipitated in an MEK/BHT
mixture as previously done. This process was repeated one more time. The polymer was

30   dried overnight in a vacuum oven at 60°C to yield 12.5 grams of a hard solid, yellow
polymer.

28

The unhydrogenated polymer (12.5 grams) was redissolved in 36 grams of tetrahydrofuran and 36 grams of methanol and 0.0625 grams of BHT for hydrogenation. Tris(triphenylphosphine) rhodium chloride [RhCl(PPh₃)] (MW= 925.27, 0.542 grams, 0.586 mmoles) catalyst was added to the polymer solution. The mixture was

5   hydrogenated in a 600 ml Parr reactor at 600 psi / 60°C for 6 hours. The reactor was cooled to ambient temperature and the pressure was vented. The solution was filtered through a fritted funnel and the powdery polymer was rinsed with acetone. The polymer was redispersed in acetone overnight. The polymer was then filtered and washed with 400 ml of acetone. The slightly yellow polymeric powder was then dried in a vacuum

10   oven overnight. 12 Grams of polymer (designated "Polymer 3") was obtained. The resulting polymer had the following molecular weights and melt flow rate: Mn=19,200, Mw=43,600, Mz=77,500, PDI= 2.3, MFI= 5.4 g/10 min with 1 wt% Ultranox 2714A (from GE Specialty Chemicals) as stabilizer.

15   Example 4.

Synthesis of Linear 5-Cycloocten-trans-1,2-diol Homopolymer and Its Saturated

Derivative (*Molecular weight control using cis-3-hexen-1-ol as chain transfer agent at a monomer / ruthenium molar ratio of 2500 and a monomer/chain transfer agent molar ratio of 260)*

20   5-Cyclooctene-trans-1,2-diol (50 grams, 0.35 moles) was transferred to a three-neck, 200 ml resin kettle equipped with a mechanical stirrer, argon inlet and a septa. The monomer was degassed under vacuum for one hour. The system was kept under an argon atmosphere. Distilled cis-3-hexen-1-ol (0.13 grams, 1.352 mmoles, 0.16 ml) was added by syringe. Methylene chloride (40 ml) was purged with a vigorous stream of

25   argon for 15 minutes and transferred via a syringe into the resin kettle. The monomer / solvent solution was stirred vigorously. In an argon filled drybox, the ruthenium catalyst, phenylmethylene bis(tricyclohexylphosphine) dichloride (0.11 grams, 0.141 mmoles) was weighed into a septum-capped glass vial and dissolved in 10 ml of methylene chloride. The deep purple catalyst solution was injected via syringe into the

30   reaction vessel. The reaction mixture was maintained at 40°C under an argon atmosphere for 24 hours under vigorous stirring. Subsequently, the resin kettle was removed from the heat source and the reaction mixture was cooled to ambient

temperature. Ethyl vinyl ether (2.92 grams, 3.9 ml, 40.4 mmoles) was added to the reaction mixture along with 100 ml of methanol, 100 ml THF and 0.5 grams of 2,6-di-tert-butyl-4-methylphenol. The polymer solution was directly hydrogenated without precipitation and recovery of the unhydrogenated polymer.

5   The hydrogenation was carried out in a 600 ml Parr reactor. 2.17 Grams (2.34 mmoles) of tris(triphenylphosphine) rhodium chloride was added to the above solution and the polymer was hydrogenated at 600 psi for 6 hours. The reactor was cooled to room temperature and vented. The resulting polymer solution was blended with 600 ml of acetone and 0.5 grams of BHT. The solution was filtered and the polymer powder

10   was washed 3 times with 200 ml of acetone. The filtered powder was resuspended in 600 ml of acetone, 0.5 grams of BHT and 0.25 ml of 2,4-pentadione and stirred overnight. The polymer dispersion was filtered and washed with three portions of 200 ml acetone. The filtered polymer was dried in a vacuum oven at 60°C for 5 hours. The resulting polymer (designated as Polymer 4) had the following molecular weights and

15   melt flow rate: $Mn= 31,300$, $Mw= 145,000$, $Mz= 269,000$, $PDI= 4.6$, $MFI=1.4$ g/10 min with 0.5 wt% sodium acetate and 0.5 wt% Ultranox 626 (from GE Specialty Chemicals) as stabilizers.

Example 5

Oxygen Transmission Rate Measurements of Linear

Ethylene-Vinyl Alcohol Copolymers

20   Table 1 describes the copolymers that were evaluated and compared.

Table 1. Description of Polymers reported in Table 2

Polymer A	A commercially obtained random, branched ethylene-vinyl alcohol copolymer. Comparative Sample (Polysciences Inc. Catalog No. 18100) containing 25 mole percent vinyl alcohol.
Polymer 1	Linear polymer with 25 mole percent vinyl alcohol units prepared via ROMP of 4-Cycloocten-1-ol followed by hydrogenation with Wilkinson's catalyst. Prepared from molar ratio of monomer to ruthenium catalyst of 400.

30

Polymer 2	Linear ethylene-vinyl alcohol copolymer containing 50 mole percent vinyl alcohol as vicinal diols prepared via ROMP of 5-cyclooctene-trans-1,2-diol followed by hydrogenation with Wilkinson's catalyst. Molecular weight controlled by monomer to ruthenium catalyst ratio of 750.
Polymer 3	Linear ethylene-vinyl alcohol copolymer containing 50 mole percent vinyl alcohol as vicinal diols prepared via ROMP of 5-cyclooctene-trans-1,2-diol followed by hydrogenation with Wilkinson's catalyst. Molecular weight controlled by monomer to ruthenium catalyst ratio of 750.
Polymer 4	Linear ethylene-vinyl alcohol copolymer containing 50 mole percent vinyl alcohol as vicinal diols prepared via ROMP of 5-cyclooctene-trans-1,2-diol followed by hydrogenation. Molecular weight controlled by use of cis-3-hexen-1-ol as chain transfer agent. Molar ratio of monomer to ruthenium catalyst was 2500 and molar ratio of monomer to chain transfer agent was 260.
Polymer B	A commercially obtained branched, random, commercial ethylene-vinyl alcohol copolymer containing 56 mole percent vinyl alcohol (Evalca E151A). Comparative Example.

Table 2. Comparison of Oxygen Gas Permeability

Sample	Description	Thickness (mils)	Oxygen Permeability (cc.mil/m^2.day.atm)	
			Dry Condition 0% Relative Humidity	Humid Condition (% RH)
Polymer A (Comp.)	EVOH (25 mole % VOH) Random, branched	6	1032	1122 (94% RH)
Polymer 1	Regio-regular Linear EVOH (25 mole % VOH)	4.2	1	46.3 (100% RH)
Polymer 2	Linear Regio-regular EVOH-(50 mole %)	1.8	0.011	0.03 (93% RH)
Polymer 3	Linear Regio-regular EVOH (50 mole %)	4.8	0.017	0.1 (96% RH)
Polymer 4	Linear Regio-regular EVOH (50 mole %)	6.1	0.029	-
Polymer B (Comp.)	EVOH (56 mole %) Random, branched	6.3	0.96	2.7 (85% RH)

...e seen from Table 2 that with either 25 or 50 mole percent vinyl alcohol ...ear regio-regular hydroxyl functionalized copolymers exhibit much ...gas barrier property both under dry and humid conditions than random, ...lymers having substantially the same vinyl alcohol molar content.

Comparison of Mechanical properties of EVOH Copolymers

	Polymer A	Polymer 1	Polymer B	Polymer 3
Vinyl	25	25	56	50
itecture:	random, branched	regio-regular linear	random, branched	regio-regular linear
ksi (sd)[*]	113 (3)	188 (11)	337 (8.7)	180 (1.1)
psi (sd)	2,395 (82)	5,161 (182)	7737 (66)	4663 (159)
% (sd)	6.7 (0.7)	4.3 (0.2)	4.3 (0.2)	5 (0.3)
psi (sd)	3,045 (110)	8,632 (835)	9093 (851)	6578 (1160)
psi (sd)	2,402 (151)	8,580 (765)	7686 (1322)	6520 (1199)
% (sd)	84 (26)	342 (11)	11.8 (8.8)	221 (34)
in.lb/in^3 (sd)	2,199 (626)	16,843 (1,368)	888 (743)	9226 (2089)

...deviation

...ear regio-regular hydroxy functionalized polymers with 25 or 50 mole ...lcohol show significantly higher strain at break and toughness than their ...terparts. The improved toughness and elongation can provide enhanced ...d thermoformability of the resultant film. Commercial branched, ... copolymers do not provide these properties.

Example 6.

Synthesis of Ethylene-Vinyl Acetate Diblock Copolymer

...mL resin kettle was equipped with a mechanical stirrer, an inlet fitting for ...m application, thermocouple and a septum. The assembled reactor was back-filled with argon prior to introduction of reagents and reactants.

32

Distilled 1,5-cyclooctadiene (30 grams, MW=110.2, 0.27 mole) was transferred to the
resin kettle via syringe. Methylene chloride (40 mL) which had been sparged with
argon was syringed into the resin kettle. The mixture was stirred until homogeneous.
In a drybox, ruthenium phenylmethylene bis-(tricyclohexylphosphine) dichloride (MW

5   = 822.96, 0.249 grams, 0.3025 mole) catalyst was weighed into a septa-capped glass
vial and dissolved in 10 mL of argon-sparged methylene chloride. The resulting deep
purple solution of catalyst was injected via syringe into the reaction vessel. The
reaction mixture was maintained with vigorous stirring under an argon atmosphere and
heated to 34°C with an oil bath. After about 40 minutes, the reaction mixture became

10   viscous. Additional methylene chloride (200 mL) was introduced into the reaction
vessel to reduce the viscosity of the mixture. After one hour, 5-acetoxycyclooct-1-ene
(6.5 grams, 0.038 mole, MW = 168.2) was injected via syringe into the vessel and the
reaction was allowed to proceed for an additional 24 hours. Toluene (200 mL) was
added to dissolve the polymer and lower the solution viscosity. Methylene chloride was

15   then removed on a rotary evaporator and the toluene/copolymer solution was transferred
to a glass-lined Parr reactor for hydrogenation. An additional 70 mL was added,
followed by grams (mole) of Wilkinson's catalyst. The reactor was pressurized to 600
psig hydrogen and heated to 60°C. The hydrogenation reaction was carried out for 6
hours under those conditions. The resultant hydrogenated copolymer was precipitated

20   and washed with acetone. The diblock copolymer was dried in a vacuum oven
overnight at 60°C and gave a white powder with the following properties: M_n = 59,400,
M_w = 107,000, M_z = 175,000, PDI = 1.8, MFI = 0.7 grams/10 min. The ethylene-vinyl
acetate diblock copolymer was found by ^{1}H NMR to contain 12.5 weight percent vinyl
acetate. The copolymer had a glass transition temperature of 34°C and melting point of

25   108°C. The block copolymer was pressed into a 6 mil clear and transparent film which
exhibited a seal strength of 6.9 (±1.3) lbs/in^2 at 120°C.


Example 7.

Synthesis of Linear Ethylene-Vinyl Alcohol Copolymer via Hydroboration/Oxidation

30   Distilled 1,5-cyclooctadiene (88.2 grams, 100 ml, 0.815 moles) was transferred
to a 1- liter round bottom flask that was evacuated and back-filled with argon.
Methylene chloride (600 mL) which had been sparged with argon was added into the

reaction flask. Ruthenium catalyst phenylmethylene bis-(tricyclohexylphosphine) dichloride (0.713 grams, 0.86 mmoles) was added, followed by vigorous stirring under an argon atmosphere. The reaction was allowed to proceed for 4 hours. Ethyl vinyl ether (0.25 grams, 3.4 mmoles) was then added to stop the reaction. The polymer was

5   isolated by precipitation in methanol and dried to yield 70.7 grams of 1,4-polybutadien. This polymer (59.4 grams) was placed in a 4-liter resin kettle and the system was purged with argon. 9-Borabicyclo[3.3.1]nonane (9-BBN, 0.5 M solution in tetrahydrofuran, 2.75 liters) was added dropwise to the kettle and the reaction mixture was stirred at 55°C for 24 hours. The solution was then chilled to about 4°C with an ice

10   bath. Degassed 6M sodium hydroxide solution (298 mL) was added dropwise to the reaction mixture. Subsequently, 609 mL of a 30 percent hydrogen peroxide solution was added very slowly to the reaction. After the addition of hydrogen peroxide was completed, the mixture was heated to 55°C for another 24 hours. The reaction mixture was cooled to ambient temperature, whereupon it separated into two layers. The THF-

15   organic layer was separated and reduced to a volume of about 1 liter using a rotary evaporator. Methanol (500 ml) was added to dissolve the polymer. The polymer solution was precipitated into 4 liters of water and was washed again 3 times with water. The viscous solid mass was then suspended in acetone and blended to break up the polymer into smaller pieces for easy work up. The polymer was recovered and

20   redissolved in a 50/50 mixture of THF/methanol and reprecipitated in water. The solid mass was blended and stirred in acetone overnight. The polymer was filtered, washed with water and dried in a vacuum oven overnight. A white solid mass, 30 grams, (designated as Polymer 5) was obtained. Polymer 5 had the following properties: M_n = 45,600, M_w = 132,000, PDI =3, MFI = 2 grams/10 min. The copolymer had a glass

25   transition temperature of 45°C and melting point of 108°C. The block copolymer was pressed into clear and transparent films. The films exhibited oxygen permeability of 1 and 15 cc.mil/m^2.day.atm at 0 and 99% relative humidity, respectively.

IN THE CLAIMS:

1.   A packaging material comprising at least one layer wherein at least one
of said layer comprises a substantially linear, regio-regular functionalized hydrocarbon
polymer having repeating units represented by the formula:

$$[-CH_2(CR_2)_a\ \underset{|}{\overset{X}{C}}H\ \underset{|}{\overset{Y}{C}}H-]$$
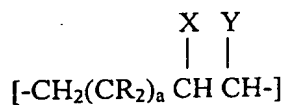
wherein

       X and Y each independently represents hydrogen, a C_1-C_3 alkyl or a functional
group selected from hydroxyl, carboxylic acid, carboxylic acid ester, acetate, amide,
nitrile or carbonyl group, provided at least one of said X and Y represents a functional
group;

       each R independently represents hydrogen or a C_1-C_5 alkyl; and

       "a" represents an integer of from 1 to 9.

2.   The packaging material of Claim 1 wherein each R represents hydrogen.

3.   The packaging material of Claim 1 wherein "a" represents an integer of
1, 2 or 4 to 9.

4.   The packaging material of Claim 2 wherein "a" represents an integer of
1, 2 or 4 to 9.

5.   The packaging material of Claim 1 wherein "a" represents an integer of
1, 2, 5, 7 or 9.

6.   The packaging material of Claim 1 wherein X and Y are each
independently selected from hydrogen atom, hydroxyl group. carboxylic acid group,
carboxylic acid ester of a C_1-C_5 alkyl, acetate group, amide group, nitrile group, or
carbonyl group.

35

7.   The packaging material of Claim 2 wherein X and Y are each independently selected from hydrogen atom, hydroxyl group, carboxylic acid group, carboxylic acid ester of a C_1-C_5 alkyl, acetate group, amide group, nitrile group, or
5   carbonyl group.

8.   The packaging material of Claim 3 wherein X and Y are each independently selected from hydrogen atom, hydroxyl group, carboxylic acid group, carboxylic acid ester of a C_1-C_5 alkyl, acetate group, amide group, nitrile group, or
10   carbonyl group.

9.   The packaging material of Claim 4 wherein X and Y are each independently selected from hydrogen atom, hydroxyl group, carboxylic acid group, carboxylic acid ester of a C_1-C_5 alkyl, acetate group, amide group, nitrile group, or
15   carbonyl group.

10.   The packaging material of Claim 6 wherein X and Y are each independently selected from hydrogen atom or hydroxyl group, provided within each of said polymer units, one of each X and Y is a hydrogen atom and one is a hydroxyl
20   group.

11.   The packaging material of Claim 7 wherein X and Y are each independently selected from hydrogen atom or hydroxyl group, provided within each of said polymer units, one of each X and Y is a hydrogen atom and one is a hydroxyl
25   group.

12.   The packaging material of Claim 8 wherein X and Y are each independently selected from hydrogen atom or hydroxyl group, provided within each of said polymer units, one of each X and Y is a hydrogen atom and one is a hydroxyl
30   group.

13.   The packaging material of Claim 9 wherein X and Y are each independently selected from hydrogen atom or hydroxyl group, provided within each of said polymer units, one of each X and Y is a hydrogen atom and one is a hydroxyl group.

5

14.   The packaging material of Claim 6 wherein X and Y each represent a functional group selected from hydroxyl group, carboxylic acid group, carboxylic acid ester of a C_1-C_5 alkyl, acetate group, amide group, nitrile group or carbonyl group.

10   15.   The packaging material of Claim 7 wherein X and Y each represent a functional group selected from hydroxyl group, carboxylic acid group, carboxylic acid ester of a C_1-C_5 alkyl, acetate group, amide group, nitrile group or carbonyl group.

16.   The packaging material of Claim 8 wherein X and Y each represent a 15   functional group selected from hydroxyl group, carboxylic acid group, carboxylic acid ester of a C_1-C_5 alkyl, acetate group, amide group, nitrile group or carbonyl group.

17.   The packaging material of Claim 9 wherein X and Y each represent a functional group selected from hydroxyl group, carboxylic acid group, carboxylic acid 20   ester of a C_1-C_5 alkyl, acetate group, amide group, nitrile group or carbonyl group.

18.   The packaging material of Claim 6 wherein said material comprises a multi-layer material.

25   19.   The packaging material of Claim 7 wherein said material comprises a multi-layer material.

20.   The packaging material of Claim 8 wherein said material comprises a multi-layer material.

30

21.   The packaging material of Claim 9 wherein said material comprises a multi-layer material.

37

22.   The packaging material of Claim 10 wherein said material comprises a multi-layer material.

5   23.   The packaging material of Claim 11 wherein said material comprises a multi-layer material.

24.   The packaging material of Claim 12 wherein said material comprises a multi-layer material.

10

25.   The packaging material of Claim 13 wherein said material comprises a multi-layer material.

26.   The packaging material of Claim 15 wherein said material comprises a

15   multi-layer material.

27.   The packaging material of Claim 18, 19, 20, 21, 22, 23, 24, 25 or 26 wherein said material is a film having a thickness of from about 0.025 mil to about 10 mils.

20

28.   A Packaging Article having a structure comprising the packaging material of Claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25 or 26.

25   29.   A Packaging Article capable of retaining an oxygen sensitive material therein, said article having a structure comprising at least one layer wherein at least one of said layers comprises a substantially linear, regio-regular functionalized hydrocarbon polymer comprising repeating units represented by the formula:

30

$$[-CH_2(CR_2)_a \overset{\overset{\displaystyle X}{\displaystyle |}}{CH} \overset{\overset{\displaystyle Y}{\displaystyle |}}{CH}-]$$

38
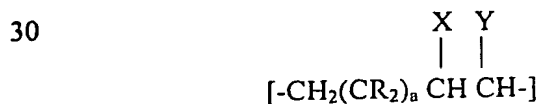
wherein each X and Y independently represents a hydrogen atom or a hydroxyl group provided at least one of said X and Y represents a hydroxyl group; R represents hydrogen or a C_1-C_5 alkyl; and "a" represents an integer of 1-9.

5   30.   The Packaging Article of Claim 29 wherein both X and Y represent hydroxyl groups.

       31.   The Packaging Article of Claim 30 wherein "a" represents an integer of 1, 2, 5, 7 or 9; and each R represents hydrogen.

10

       32.   The Packaging Article of Claim 31 wherein "a" represents 1 or 5.

       33.   The Packaging Article of Claim 29, 30, 31 or 32 wherein said article structure is a film.

15

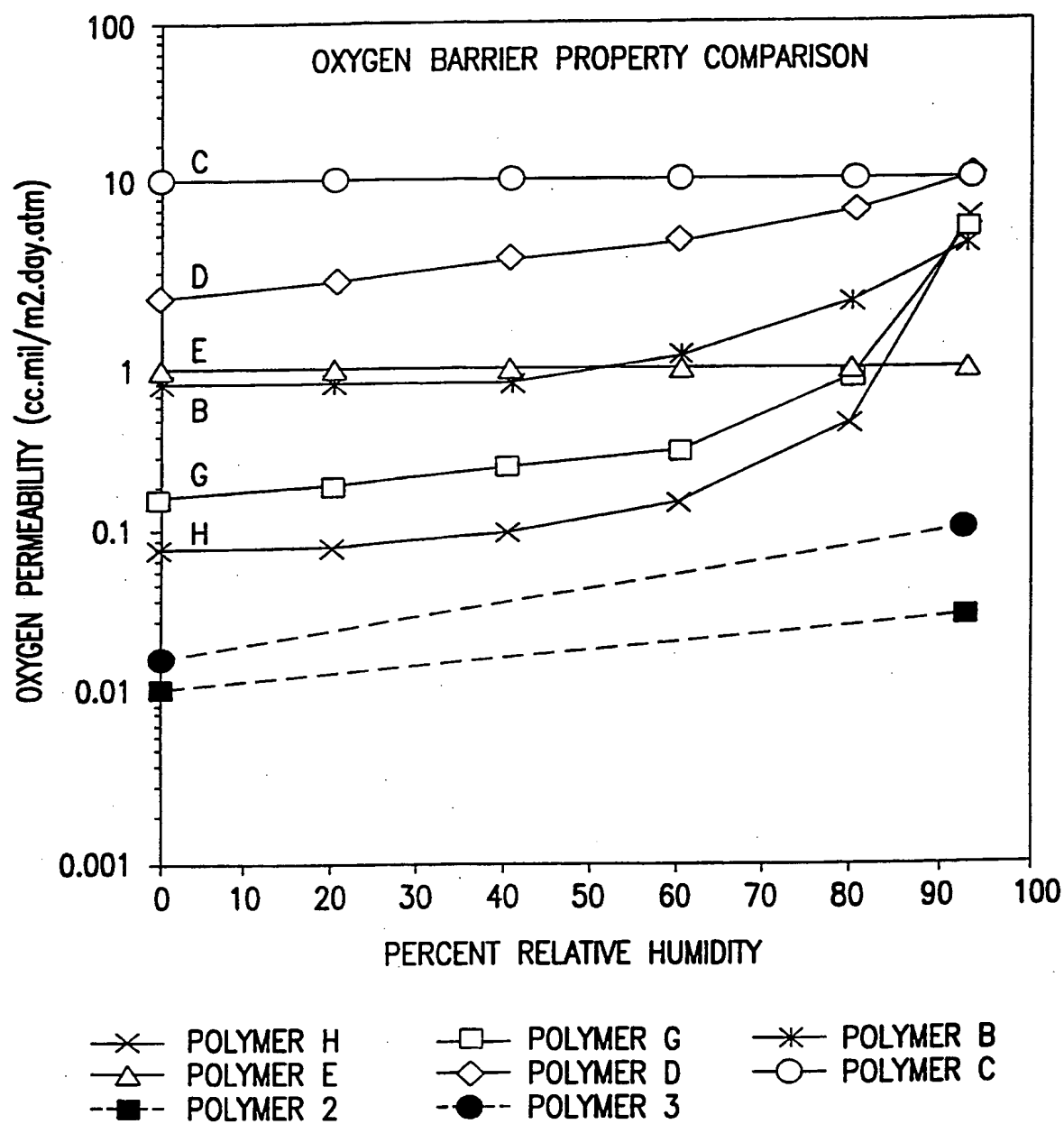   34.   The Packaging Article of Claim 33 wherein said film is a multi-layer film.

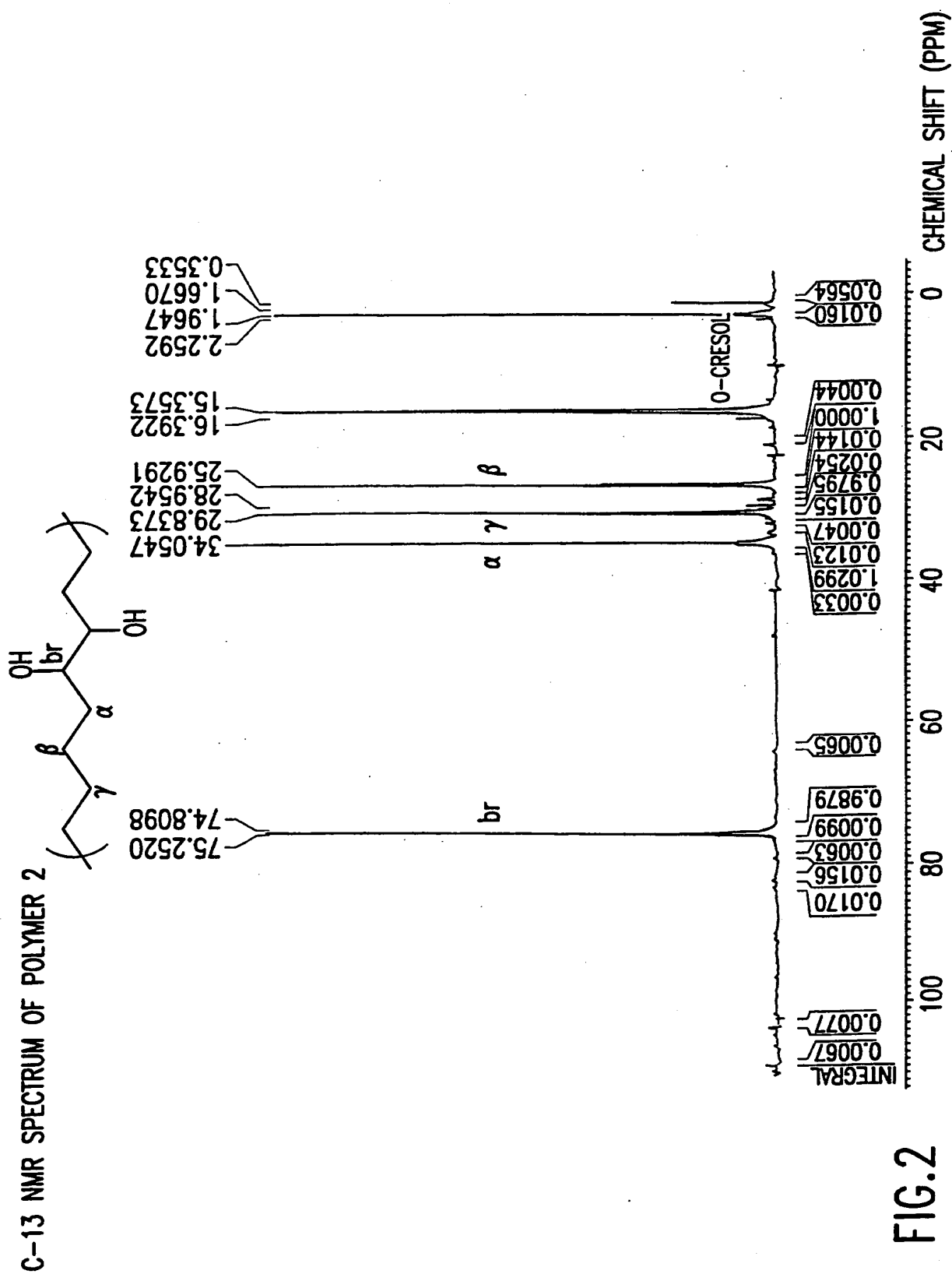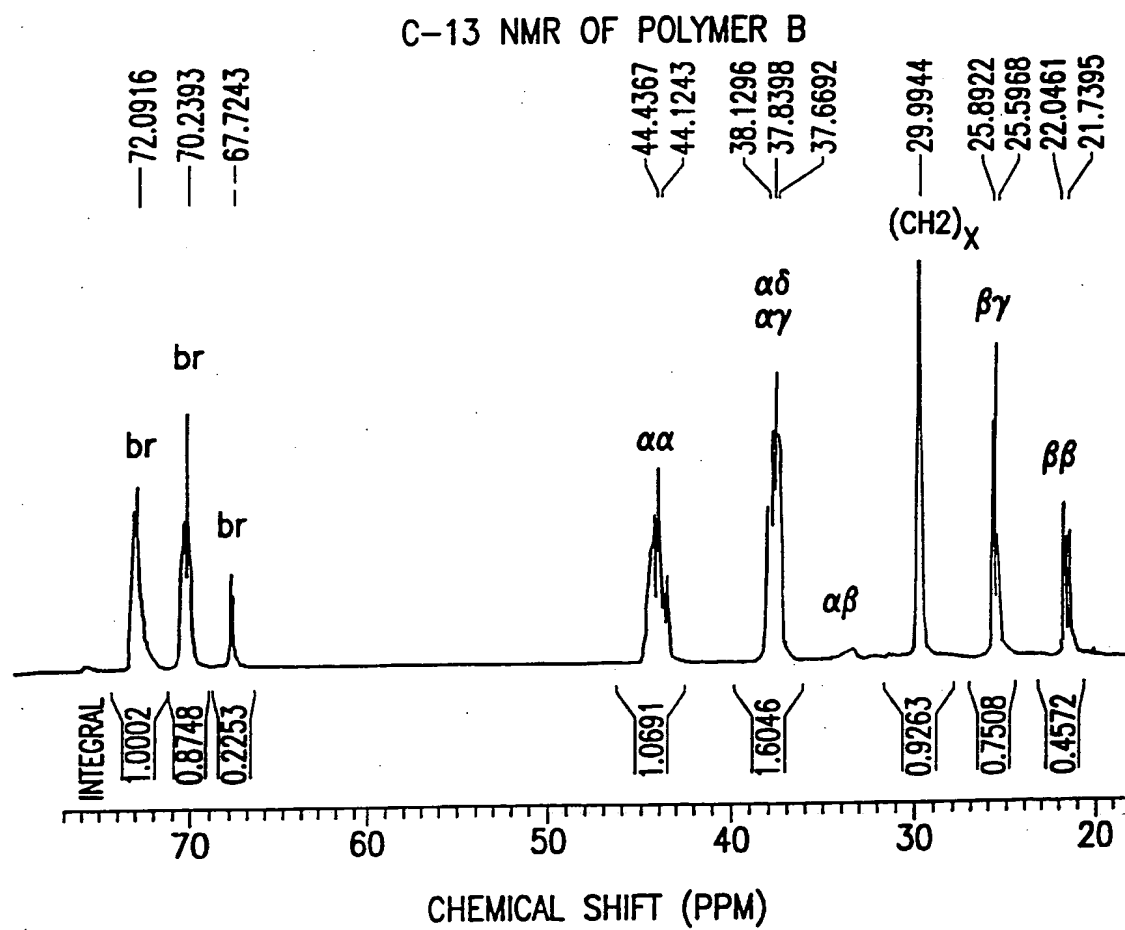FIG.1

C-13 NMR SPECTRUM OF POLYMER 2

FIG.2

C-13 NMR OF POLYMER B

CHEMICAL SHIFT (PPM)

FIG.3

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   B32B27/32   B65D65/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   C07F   B32B   B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 824 125 A (CIBA GEIGY AG) 18 February 1998 (1998-02-18) page 3, line 5-15 -page 5, line 42-50; claim 11	1,6,28, 29,33
X A	US 5 439 992 A (YI KONG S ET AL) 8 August 1995 (1995-08-08) column 14, line 47-51 -column 15, line 9-24-32	1,6,28, 29,33 27
X	WO 97 19991 A (EXXON CHEMICAL PATENTS INC) 5 June 1997 (1997-06-05) claims 1,3,4,7-9,11; examples 5,6	1-4,6-9, 28,29,33
Y	EP 0 796 607 A (IVOCLAR AG) 24 September 1997 (1997-09-24) page 3-5; claims 1-4,6,7	1,6,14, 28,29

-/--

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the International filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the International filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the International search

14 February 2000

Date of mailing of the International search report

29. 02. 2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL – 2280 HV Rijswijk
Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,
Fax: (+31–70) 340–3016

Authorized officer

Derz, T

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INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 20865 A (ADVANCED POLYMER TECHNOLOGIES) 12 June 1997 (1997-06-12) page 6, line 19-30; claims 32-34,37-39,43	1,6,28, 29
Y	EP 0 626 402 A (AMOCO CORP) 30 November 1994 (1994-11-30) page 7; claims 1-3,5,9	1,6,29
X	US 5 529 833 A (ROBERTS WILLIAM P ET AL) 25 June 1996 (1996-06-25) cited in the application	1-13, 18-25, 27-29, 33,34
Y	column 7, line 17 -column 8, line 41-49; claims 1,5 column 9, line 67 -column 12, line 22-67	1,6,14, 28,29

2

| **Box I** | **Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)** |

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: **1, 6, 29 (all partly)**
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

| **Box II** | **Observations where unity of invention is lacking (Continuation of item 2 of first sheet)** |

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

INTERNATIONAL SEARCH REPORT

FURTHER INFORMATION CONTINUED FROM   PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1, 6, 29 (all partly)

Present independent claims 1 and 29 relate to an extremely large number
of possible products comprising the polymers defined by the Markush
formula. Support within the meaning of Article 6 PCT and disclosure
within the meaning of Article 5 PCT is to be found, however, for only a
very small proportion of the products claimed. In the present case, the
claims so lack support, and the application so lacks disclosure, that a
meaningful search over the whole of the claimed scope is impossible.
Consequently, the search has been carried out for those parts of the
claims which appear to be supported and disclosed, namely those parts
relating to the products:

the search has been restricted to R1 or R2 or X or Y = C1-3 alkyl and/or
hydroxyl whereby R1 + R2 together can form a bridging group,
i.e. functionalized cycloolefinic copolymers (ring-opened COC, as in the
examples, which have only hydroxyl and acetate (ex. 6) as functional
groups, prepared by the ROMP method as well) have been searched for use
in packaging applications. X and/or Y = nitrile, carbonyl and ester were
found.
StereoREGULAR (isotactic, syndiotactic = 'regio regular') PP, 4-MP-1 etc.
falling under the formula of claim 1 have been searched. EVOH was found
in the cited prior art.
The co-pending US serial 09/052079, published as WO99/50331 on 7 October
1999, thus after the filing date of the present application. The
application '079 ('incorporated by') does not support the disclosure of
claim 1 or formula I), but only of the ring-opened educts of formula
(II), leading to the polymer products of formulas (IV) and (V) with
NON-geminal R's.

Present claims 1, 6 and 29 further relate to an extremely large number of
possible products. In fact, the claims contain so many options and
possible permutations with one only OPTIONAL proviso (cf. claims 1 and
29) that a lack of clarity within the meaning of Article 6 PCT arises to
such an extent as to render a meaningful search of the claims impossible.

The initial phase of the search revealed further a very large number of
documents relevant to the issue of novelty. So many documents were
retrieved that it is impossible to determine which parts of the claim(s)
may be said to define subject-matter for which protection might
legitimately be sought (Article 6 PCT). For these reasons, a meaningful
search over the whole breadth of the claim(s) is impossible.
Consequently, the search has been restricted to R1 or R2 or X or Y =
C1-3 alkyl and/or hydroxyl whereby R1 + R2 together can form a bridging
group.

In conclusion: the independent claims 1 and esp. 29 are too broad to be
supported:
(I) From EVOH (!, because the term 'regio-regular' is unclear;
polyethylene excluded by proviso of ONLY claim 1, not claim 6, cf. below)
to more complicated polymers of the MARKUSH formula above, millions of

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

polymers are claimed in the application packaging materials;
(II) There is No relation between claim 1 and the method of making (ROMP) in the description;
(III) Lack of disclosure, ex. 2-4 disclose X Y= OH, ex. 6: X Y= acetate, (ex. for other X's, Y's referred to in claim 1 are missing);
(IV) Lack of support (comp. claim 1 => formula (I) with formulas (IV) and (V), it is not the same position of R's (geminal vs. 1-4 position)) => unclarity, Art. 84 EPC;
(V) all examples are based ONLY on ROMP linear (4- or 5-) Cycloocten-(1- or 1,2-di)-ol saturated homopolymers, cf. formulas (IV) and (V), they are NOT examples for claim 1 with R's other than 'H';
(VI) Essential feature(s) missing: O2-barrier property (much better than of EVOH);
(VII) Art. 84 EPC objection vs. claim 6 due to unclarity: the proviso is overruled, therefore a de-facto independent claim equal to independent claim 29 is created, if it is not an undue repetition of wording of claim 1.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

Int. ional Application No

PCT/US 99/21826

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0824125	A	18-02-1998	JP	10087793 A	07-04-1998
US 5439992	A	08-08-1995	US	5319034 A	07-06-1994
			US	5206306 A	27-04-1993
			US	5115041 A	19-05-1992
			AU	2655095 A	04-01-1996
			DE	69505812 D	10-12-1998
			DE	69505812 T	27-05-1999
			EP	0764181 A	26-03-1997
			JP	10502393 T	03-03-1998
			WO	9533786 A	14-12-1995
			US	5705572 A	06-01-1994
			CA	2008779 A	30-09-1990
			CN	1047097 A,B	21-11-1990
			EP	0395885 A	07-11-1990
			JP	2286712 A	26-11-1990
			MX	170348 B	17-08-1993
			NO	900254 A	01-10-1993
WO 9719991	A	05-06-1997	BR	9611669 A	23-02-1999
			CA	2234108 A	05-06-1997
			CN	1203614 A	30-12-1998
			EP	0863943 A	16-09-1998
EP 0796607	A	24-09-1997	DE	19616183 A	25-09-1997
			CA	2199567 A	20-09-1997
			JP	10030018 A	03-02-1998
WO 9720865	A	12-06-1997	US	5939504 A	17-08-1999
			AU	1277197 A	27-06-1997
			CN	1208421 A	17-02-1999
			EP	0865449 A	23-09-1999
			AU	2120697 A	28-08-1997
			CN	1215411 A	28-04-1999
			EP	0879251 A	25-11-1998
			WO	9729135 A	14-08-1997
EP 0626402	A	30-11-1994	US	5403904 A	04-04-1995
			US	5519101 A	21-05-1996
			US	5512635 A	30-04-1996
			CA	2123843 A	28-11-1996
			US	5589548 A	31-12-1996
			US	5559190 A	24-09-1996
			US	5621047 A	15-04-1997
			US	5589543 A	31-12-1996
			US	5731383 A	24-03-1998
US 5529833	A	25-06-1996	US	5350622 A	27-09-1994
			AU	657728 B	23-03-1995
			AU	1141092 A	08-10-1992
			CA	2062083 A	03-10-1992
			CS	9201000 A	14-10-1992
			EP	0507207 A	07-10-1992
			FI	921425 A	03-10-1992
			HU	67219 A	28-03-1995
			IL	101161 A	14-05-1996
			JP	5115776 A	14-05-1993
			MX	9201379 A	01-10-1992

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5529833 A		NO 921268 A	05-10-1992
		NZ 241802 A	22-12-1994
		PL 171849 B	30-06-1997
		PL 172483 B	30-09-1997
		RU 2092513 C	10-10-1997
		US 5346644 A	13-09-1994
		US 5700554 A	23-12-1997
		ZA 9201914 A	16-09-1993